Hartree Algorithm
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Abstract

The self-compatible Hartree method is used in atomic physics to determine the energy levels of many-electron atoms. In this work we extend this procedure to electrons moving in the Coulomb field of a distribution of positive ions in a Bravais lattice.

1 Problem Setup

$N^{(\text{ion})}$ = number of positive ions (each with nuclear charge $+Ze$) of a Born-Von Karman domain Σ_α relative to a Bravais lattice Σ_∞. If $0 < z \le Z$ is the degree of ionization of a single ion, the number of electrons in Σ_α is $N^{(\text{el})} = N^{(\text{ion})}z$. In the Born-Oppenheimer approximation [1] and abstracting from the spin, i.e. taking into account only the orbital degrees of freedom, the Hilbert space associated with the system is $\mathcal{H}_e = \mathcal{L}^2\left(\mathbb{R}^{3N^{(\text{el})}}\right)$. In the non-relativistic limit the Hamiltonian is

$$\hat{H}_e = \hat{T}_e + \hat{U}_{en} + \hat{U}_{ee} \tag{1}$$

having used the symbol U for the potential energy, since with V we have denoted the volume of the BVK domain. The kinetic energy operator is with obvious meaning of the symbols:

$$\hat{T}_e = \sum_{j=1}^{N^{(\text{el})}} \frac{\hat{\mathbf{p}}_j^2}{2m_e} \tag{2}$$

We write this operator in the coordinate representation i.e. in the basis $\{|\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\rangle\}$ where $|\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\rangle$ is the generic eigenket of the position. Precisely, we have the eigenvalue equation:

$$\hat{\mathbf{r}}_j \left|\mathbf{r}_1, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1,...,}\mathbf{r}_{N^{(\text{el})}}\right\rangle = \mathbf{r}_j \left|\mathbf{r}_1, ..., \mathbf{r}_{j-1}, \mathbf{r}_{j+1,...,}\mathbf{r}_{N^{(\text{el})}}\right\rangle, \quad j = 1, 2, ..., N^{(\text{el})}$$

with $\mathbf{r}_j = (x_j, y_j, z_j)$ that is, the eigenvalue of the position observable for the j-th electron. Since this is an orthonormal basis

$$\left\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}} | \mathbf{r}_1', \mathbf{r}_2', ..., \mathbf{r}_{N^{(\text{el})}}' \right\rangle = \prod_{j=1}^{N^{(\text{el})}} \delta^{(3)}\left(\mathbf{r}_j - \mathbf{r}_j'\right)$$

Completeness is expressed as:

$$\int_{\mathbb{R}^{3N^{(\text{el})}}} \prod_{j=1}^{N^{(\text{el})}} d^3 r_j \left|\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\right\rangle \left\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\right| = \hat{1}$$

It follows

$$|\Psi\rangle = \int_{\mathbb{R}^{3N^{(\text{el})}}} \prod_{j=1}^{N^{(\text{el})}} d^3 r_j \left|\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\right\rangle \underbrace{\left\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}} | \Psi \right\rangle}_{=\Psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\right)}, \quad \forall |\Psi\rangle \in \mathcal{H}_e$$

As is known, the representation of the impulse operator $\hat{\mathbf{p}}_j$ in the basis $\{|\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}}\rangle\}$ is:

$$\langle \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\text{el})}} | \hat{\mathbf{p}}_j | \Psi \rangle = -i\hbar \boldsymbol{\nabla}_{\mathbf{r}_j} \Psi$$

where $\boldsymbol{\nabla}_{\mathbf{r}_j} = \left(\frac{\partial}{\partial x_j}, \frac{\partial}{\partial y_j}, \frac{\partial}{\partial z_j}\right)$. Compact notation is usually used $\hat{\mathbf{p}}_j \doteq -i\hbar \boldsymbol{\nabla}_{\mathbf{r}_j}$, where $\doteq$ stands for "represented by". (2) becomes:

$$\hat{T}_e \doteq -\sum_{j=1}^{N^{(\mathrm{el})}} \frac{\hbar^2}{2m_e} \boldsymbol{\nabla}_{\mathbf{r}_j}^2 \tag{3}$$

We make the remaining terms explicit in (1). The potential energy of interaction between electrons and nuclei/ions is

$$U_{en}\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right) = -\sum_{\mathbf{R} \in \Sigma_\alpha} \sum_{j=1}^{N^{(\mathrm{el})}} \frac{Ze^2}{|\mathbf{r}_j - \mathbf{R}|} \tag{4}$$

That is, the electrons move in the field of Coulomb forces exerted by the ions, of potential energy (4).

Notation 1 *Some authors use the term "potential" instead of "potential energy". As is known, these are two different quantities. We will use the second and occasionally the first.*

The Coulomb repulsion between electrons is a force field of potential energy:

$$U_{ee}\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right) = \frac{1}{2} \sum_{\substack{j,l=1 \\ j \neq l}}^{N^{(\mathrm{el})}} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_l|} \tag{5}$$

where $1/2$ is necessary because the terms of the sum are repeated twice. The representation of the Hamiltonian (1) in the coordinate basis is written:

$$\hat{H}_e = -\sum_{j=1}^{N^{(\mathrm{el})}} \frac{\hbar^2}{2m_e} \boldsymbol{\nabla}_{\mathbf{r}_j}^2 - \sum_{\mathbf{R} \in \Sigma_\alpha} \sum_{j=1}^{N^{(\mathrm{el})}} \frac{Ze^2}{|\mathbf{r}_j - \mathbf{R}|} + \frac{1}{2} \sum_{\substack{j,l=1 \\ j \neq l}}^{N^{(\mathrm{el})}} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_l|} \tag{6}$$

As in all non-relativistic quantum mechanics problems, it is a matter of solving the spectrum of the operator (<ref>eq:he1</ref>) i.e. solving the eigenvalue equation:

$$\hat{H}_e \left| E \right\rangle = E \left| E \right\rangle$$

which in the language of wave functions (eigenfunctions of energy) returns the time-independent Schrödinger equation for the system of $N^{(\mathrm{el})}$ electrons:

$$-\sum_{j=1}^{N^{(\mathrm{el})}} \frac{\hbar^2}{2m_e} \boldsymbol{\nabla}_{\mathbf{r}_j}^2 \psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right) - \sum_{\mathbf{R} \in \Sigma_\alpha} \sum_{j=1}^{N^{(\mathrm{el})}} \frac{Ze^2}{|\mathbf{r}_j - \mathbf{R}|} \psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right) + \tag{7}$$

$$+\frac{1}{2} \sum_{\substack{j,l=1 \\ j \neq l}}^{N^{(\mathrm{el})}} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_l|} \psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right) = E\psi\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right)$$

which cannot even be solved numerically.

2 Hartree Algorithm

Hartree uses the independent electron approximation in the sense that the Hamiltonian of the system factorizes as follows:

$$\hat{H}_e = \sum_{j=1}^{N^{(el)}} \hat{H}_j \tag{8}$$

where $\hat{H}_j$ is the Hamiltonian of the j-th electron. Denoting with $(\mathbf{r}, \mathbf{p})$ the position and momentum variables for this electron, we have:

$$\hat{H}_j (\mathbf{r}, \mathbf{p}) = \frac{\hat{\mathbf{p}}^2}{2m_e} + U_j (\hat{\mathbf{r}}) \implies \hat{H}_j (\mathbf{r}, \mathbf{p}) \doteq -\frac{\hbar^2}{2m_e} \nabla^2 + U_j (\mathbf{r}) \tag{9}$$

from which we see that in our numbering of electrons, we label only the Hamiltonian and the potential energy, leaving the position and momentum variables free. (8) implies that the Hilbert space associated with the electron system $\mathcal{H}_e = \mathcal{L}^2 \left(\mathbb{R}^{3N^{(el)}} \right)$ is

$$\mathcal{H}_e = \bigotimes_{j=1}^{N(el)} \mathcal{H}_j, \quad \mathcal{H}_j = \mathcal{L}^2 \left(\mathbb{R}^3 \right) \tag{10}$$

The j-th electron moves in the electric field generated by the ions and the remaining $N^{(el)} - 1$ electrons. The potential energy $U_j (\mathbf{r})$ is written:

$$U_j (\mathbf{r}) = U_j^{(ion)} (\mathbf{r}) + U_j^{(el)} (\mathbf{r}) \tag{11}$$

having separated the contribution of the ions from that of the remaining electrons. The first is given by

$$U_j^{(ion)} (\mathbf{r}) = -\sum_{\mathbf{R} \in \Sigma_\alpha} \frac{Ze^2}{|\mathbf{r}_j - \mathbf{R}|} \tag{12}$$

The potential energy $U_j^{(el)} (\mathbf{r})$ can be expressed by the potential $\Phi_j^{(el)} (r)$ of the electric field of the remaining electrons, exerted on the j-th electron:

$$U_j^{(el)} (\mathbf{r}) = -e\Phi_j^{(el)} (\mathbf{r}) \tag{13}$$

From electrostatics [2]:

$$\Phi_j^{(el)} (\mathbf{r}) = \int_{D(\Sigma_\alpha)} \frac{\rho_j (\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r'$$

where $D (\Sigma_\alpha)$ is any domain containing Σ_a, it is usually assumed $D (\Sigma_\alpha) = \mathbb{R}^3$:

$$\Phi_j^{(el)} (\mathbf{r}) = \int_{\mathbb{R}^3} \frac{\rho_j (\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3 r' \tag{14}$$

while $\rho_j (\mathbf{r})$ is the electric charge density of the system of $N^{(el)} - 1$ electrons.

$$\rho_j (\mathbf{r}) = \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \rho_l (\mathbf{r}) \tag{15}$$

If $\psi_l(\mathbf{r})$ is the generic eigenfunction of $\hat{H}_l$, we have $\rho_l(\mathbf{r}) = -e|\psi_l(\mathbf{r})|^2$. Therefore

$$\Phi_j^{(el)}(\mathbf{r}) = -e \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{|\psi_l(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d^3 r' \tag{16}$$

which replaced in (13)

$$U_j^{(el)}(\mathbf{r}) = e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{|\psi_l(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d^3 r' \tag{17}$$

We are finally able to write the single electron Hamiltonian:

$$\hat{H}_j = \underbrace{-\frac{\hbar^2}{2m_e}\nabla^2 + U_j^{(ion)}(\mathbf{r})}_{\hat{H}_{Block}} + e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{|\psi_l(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d^3 r' \tag{18}$$

where we have highlighted the Bloch Hamiltonian [3] in which the potential energy is periodic with period given by the individual lattice steps a_i (con $i = 1, 2, 3$). The additional term that takes into account the Coulomb interaction with the remaining electrons is the *Hartree potential*:

$$U_H(\mathbf{r}) = e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{|\psi_l(\mathbf{r})|^2}{|\mathbf{r}-\mathbf{r}'|} d^3 r' \tag{19}$$

which destroys the periodicity and hence the invariance under discrete translations of step a_i. Let's set the eigenvalue problem:

$$\hat{H}_j|\varepsilon_j\rangle = \varepsilon_j \hat{H}_j|\varepsilon_j\rangle \tag{20}$$

In the representation of coordinates it is $\psi_j(\mathbf{r}) = \langle\mathbf{r}|\varepsilon_j\rangle$, for which (20) for $j = 1, 2, ..., N^{(el)}$:

$$-\frac{\hbar^2}{2m_e}\boldsymbol{\nabla}^2 \psi_j(\mathbf{r}) + U_j^{(ion)}(\mathbf{r})\psi_j(\mathbf{r}) + \tag{21}$$

$$+ \left[e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{|\psi_l(r)|^2}{|\mathbf{r}-\mathbf{r}'|} d^3 r' \right] \psi_j(\mathbf{r}) = \varepsilon_j \psi_j(\mathbf{r}), \quad (j = 1, 2, ..., N^{(el)})$$

(21) constitute a system of $N^{(el)}$ nonlinear integro-differential equations in the unknown functions $\psi_j(\mathbf{r})$. These equations are coupled: the coupling expresses the Coulomb interaction between the electrons. (10) implies

$$\psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(el)}}) = \prod_{j=1}^{N^{(el)}} \psi_j(\mathbf{r}), \quad E = \sum_{j=1}^{N^{(el)}} \varepsilon_j \tag{22}$$

Apparently we have not made any progress. In fact, the problem has become more complicated because we have gone from a linear differential equation in a function ψ (unknown) of $3N^{(el)}$ real variables, to $N^{(el)}$ nonlinear integro-differential equations! And this is where the Hartree algorithm comes into play, which consists in proceeding by successive approximations, and the corresponding iterations linearize the equations. In zero approximation, a set of trial functions $\psi_j^{(0)}(\mathbf{r})$ are assumed

as solutions of (21). The decomposition of the single-electron Hamiltonian (18) that we report here in compact form

$$\hat{H}_j = \hat{H}_{Block} + \hat{U}_H(\mathbf{r})$$ (23)

suggests to take as $\psi_j^{(0)}(\mathbf{r})$, the *crystal orbitals* i.e. the Bloch eigenfunctions. Then we calculate

$$U_H^{(0)}(\mathbf{r}) = e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{\left|\psi_l^{(0)}(\mathbf{r})\right|^2}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$ (24)

to be replaced in (21):

$$-\frac{\hbar^2}{2m_e}\boldsymbol{\nabla}^2\psi_j(\mathbf{r}) + U_j^{(ion)}(\mathbf{r})\psi_j(\mathbf{r}) + U_H^{(0)}(\mathbf{r})\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r}), \quad (j=1,2,...,N^{(el)})$$ (25)

which is a system of $N^{(el)}$ Schrödinger equations and as such solvable (at least in principle). The corresponding solutions are nothing other than the solutions of (21) in approximation 1 and which we denote with $\psi_j^{(1)}(\mathbf{r})$, $\varepsilon_j^{(1)}$. These allow us to calculate the Hartree potential in approximation 1:

$$U_H^{(1)}(\mathbf{r}) = e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{\left|\psi_l^{(1)}(\mathbf{r})\right|^2}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$ (26)

to replace in (21), obtaining the system:

$$-\frac{\hbar^2}{2m_e}\boldsymbol{\nabla}^2\psi_j(\mathbf{r}) + U_j^{(ion)}(\mathbf{r})\psi_j(\mathbf{r}) + U_H^{(1)}(\mathbf{r})\psi_j(\mathbf{r}) = \varepsilon_j\psi_j(\mathbf{r}), \quad (j=1,2,...,N^{(el)})$$ (27)

whose solutions of (21) in approximation 2 and which we denote by $\psi_j^{(2)}(\mathbf{r})$, $\varepsilon_j^{(2)}$. These allow us to calculate the Hartree potential in approximation 2:

$$U_H^{(2)}(\mathbf{r}) = e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{\left|\psi_l^{(2)}(\mathbf{r})\right|^2}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$ (28)

By repeating the procedure, we obtain the solutions of the (21) in order approximation $s > 2$:

$$\psi_j^{(s)}(\mathbf{r}), \ \varepsilon_j^{(s)}$$

and then

$$U_H^{(s)}(\mathbf{r}) = e^2 \sum_{\substack{l=1 \\ l \neq j}}^{N^{(el)}-1} \int_{\mathbb{R}^3} \frac{\left|\psi_l^{(s)}(\mathbf{r})\right|^2}{|\mathbf{r}-\mathbf{r}'|} d^3r'$$ (29)

and so on. The process stops at one step $s_0 \in \mathbb{N}$ such that:

$$\psi_j^{(s_0)}(\mathbf{r}) \simeq \psi_j^{(s_0-1)}(\mathbf{r}), \ \varepsilon_j^{(s_0)} \simeq \varepsilon_j^{(s_0-1)}, \ U_H^{(s_0)}(\mathbf{r}) \simeq U_H^{(s_0-1)}(\mathbf{r})$$

where $\simeq$ refers to the required precision. The condition $U_H^{(s_0)}(\mathbf{r}) \simeq U_H^{(s_0-1)}(\mathbf{r})$ is expressed by saying that the potential $U_H^{(s_0)}(\mathbf{r})$ is *self-compatible* (*or self-consistent*).

3 Physical interpretation

From the above, Hartree reduces the potential energy to many bodies

$$U\left(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N^{(\mathrm{el})}}\right) = -\sum_{\mathbf{R} \in \Sigma_\alpha} \sum_{j=1}^{N^{(\mathrm{el})}} \frac{Ze^2}{|\mathbf{r}_j - \mathbf{R}|} + \frac{1}{2} \sum_{\substack{j,l=1 \\ j \neq l}}^{N^{(\mathrm{el})}} \frac{e^2}{|\mathbf{r}_j - \mathbf{r}_l|}$$

to an effective potential energy in which the single electron moves, which is given by the sum of the potential energy exerted by the ions and the potential energy U_H which is the average effect exerted on an electron by the remaining electrons of the solid.

References

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